

Ammonia activation on platinum {111}: A density functional theory study

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Abstract

By means of density functional theory calculations we have investigated the role of adsorbed atomic oxygen and adsorbed OH in the oxidation of ammonia on Pt{111}. We have investigated the dissociation of $\text{NH}_{3,\text{ads}}$, $\text{NH}_{2,\text{ads}}$ and NH_{ads} on Pt{111} and the oxidation of these species by O_{ads} and OH_{ads} . We have done normal mode frequency analysis and work function calculations to characterise reactant, product and transition states. We have determined reaction energies, activation entropies, kinetic parameters and corrected total energies with the zero point energy. We have shown that O_{ads} only activates the dehydrogenation of $\text{NH}_{3,\text{ads}}$ and that OH_{ads} activates the dehydrogenation of all $\text{NH}_{x,\text{ads}}$ species and have reasoned this difference in activation by a bond order conservation principle. We have pointed out the importance of a zero point energy correction to the reaction energies and barriers. We have compared the calculated vibrational modes of the adsorbates with corresponding experimental EELS data. This has led to a revise of the frequency assignment of $\nu(\text{Pt-OH}_2)$, a revise in the identification of a NH_2 species on the Pt{111} surface after electron bombardment of pre-adsorbed NH_3 and the confirmation of an ammonia dimer binding model at the expense of a hollow site occupation by ammonia on the Pt{111} surface.

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1. Introduction

At the beginning of the 20th century, chemists solved the difficult problem to transform dinitrogen from the air to bound nitrogen in ammonia and nitrates at a large scale. It was made possible by the Haber-Bosch ($\text{N}_2 + \text{H}_2 \rightarrow \text{NH}_3$) and the Ostwald process ($\text{NH}_3 + \text{O}_2 \rightarrow \text{NO} \rightarrow \text{HNO}_3$) [1,2]. It had a tremendous impact on chemical reactor engineering, agriculture and world's history in general. High pressure plants, artificial fertilisers and ammunition production are keywords in this context. Although the Ostwald process is so important and a highly optimised indus-

trial process, it is far from being understood on a microscopic level.

It is somewhat ironic to conclude that, contrary to producing NH_3 and NO from N_2 , chemists also take effort to find processes that convert ammonia and NO “back” to N_2 . Ammonia is a toxic component in gaseous and aqueous waste streams and its decomposition to N_2 is therefore a prominent topic in environmental catalysis. There is an increasing interest in oxidising ammonia using metallic and oxidic catalysts in water. This can take place electrochemically and using oxygen as oxidising agent [3,4]. Ammonia is also used in industry to reduce NO_x emissions in the so called selective catalytic reduction process (SCR) [5]. This reaction requires excess NH_3 . The unreacted ammonia is present in the off-gas and must be removed in a secondary step. The selective catalytic oxidation

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(SCO) of ammonia by dioxygen to dinitrogen and water is of special interest in this respect.

Depending on the reaction conditions the oxidation of ammonia can lead to formation of H_2O , H_2 , N_2 , NO , N_2O . It can be accompanied with a high faceting of the Pt surface at higher pressures and temperatures. Most research concentrates on the reasoning of the pronounced product selectivity towards N_2 and NO . High-temperatures and high oxygen coverages lead to preferably NO production. Industrially it is even possible to transform ammonia into NO almost quantitatively. Low-temperatures and high ammonia coverages lead to preferably N_2 and possibly N_2O production. At higher pressures N_2O production competes with N_2 production, but N_2O formation has never been observed at low pressure surface science conditions.

Single crystal studies concentrate on the analysis of the product composition in relation to reactant composition, surface condition and surface intermediates [6–12]. The results confirm the pronounced product selectivity towards N_2 or NO dependent on temperature and oxygen coverage. N , NH , NH_2 , O , OH and NO are detected as intermediates on the surface. The Pt{100} surface is more active than the (111) facet and shows a preference for NO production. The preferred bridge site occupation of oxygen on Pt{100} might be important in this respect [13]. Also the low barrier for the $\text{N}_{\text{ads}} + \text{O}_{\text{ads}}$ reaction on Pt{100} may be important [14]. Proposed ammonia activation mechanisms usually include some stripping of hydrogen from ammonia and its fragments by O_{ads} or OH_{ads} , N_2 formation by atomic nitrogen combination, NO formation by the combination of atomic nitrogen and atomic oxygen or $\text{NH}_{\text{ads}} + \text{O}_{\text{ads}}$. H_2O formation occurs by either $\text{NH}_x + \text{OH}_{\text{ads}}$ or OH recombination or both. Surface restructuring is obviously present during reaction condition, but is not explicitly considered in any of the mechanistic studies. Intermediates have been proposed mainly based on detection by spectroscopy.

The different reaction steps that lead to N_2 are summarised in the kinetic scheme of Fig. 1. Since NO is strongly adsorbed, N_2O product formation below the desorption temperature of NO is a signature of intermediate NO formation. It is an important product in high pressure studies on Pt powders. A theoretical study of reaction r_3 catalysed by Pt{211} has been published by Hu et al. [15]. In this study N_2O formation was shown to be strongly surface dependent. The recombination of two NO molecules was found to be preferred over reaction of NO_{ads} with N_{ads} . On Cu–Ag catalysts with an oxidic overlayer reaction path

(1b) has been shown to dominate [16]. On Pt there is no conclusive evidence on the relative importance of reaction 1b.

The dehydrogenation reactions of NH_x by O_{ads} and OH_{ads} are part of most proposed reaction mechanisms of ammonia oxidation on platinum. Despite this, little is known about the energetics and kinetics of these reaction steps. In the present theoretical study, we want to elucidate this and focus on the oxidation of ammonia catalysed by the Pt{111} surface. In particular we address the question of the role of adsorbed O and OH in the activation of NH_x species. These processes are behind the reaction steps denoted with r_1 and r_2 in the reaction scheme (Fig. 1). For completeness also the recombinative desorption of N_2 and NO are included. Previously we have shortly published the activation barriers and energy changes of the dehydrogenation reaction of ammonia, that indicated the important role of oxygen in the activation of ammonia [17]. In this paper we elaborate on these results. We will characterise adsorbates in detail. We will include zero point energy correction to the activation barriers, present exponential pre-factors of reaction rate constants and make entropy considerations. In a consecutive paper the oxidation of ammonia catalysed by stepped surfaces as Pt{211} will be analysed.

The article is organised in the following manner. After the introduction we will describe the model, method and computational details of our investigations. Then we will deal with energetics and dynamics of the possible reactants, intermediates and products of the ammonia oxidation steps on Pt{111}. We will present the preferred binding sites, energies and a normal mode frequency analysis (NMFA) of the adsorption states. If possible we will compare our results of the (co-)adsorbates with previous work and try to give a consistent picture of the new and old findings. In the section thereafter we will study the kinetics of the reactions. We will point out the importance of a zero point energy correction of the states. We will give an estimate of the pre-exponential factor, activation energy and entropy of the dehydrogenation reactions. We will complete the ammonia oxidation reaction on Pt{111} with the $\text{N} + \text{N}$ and $\text{N} + \text{O}$ (re)combination reaction.

2. Model, method and computational details

The Pt{111} surface has been modelled by a supercell approach. A 2×2 unit-cell consisting of five layers of Pt atoms in a fcc layering and separated by five metal layers replaced by vacuum (13.8 Å) has been periodically expanded into space. The so formed Pt{111} slab consists of closed packed atoms, which form a honeycomb structured surface. The layering of the metal atoms, give rise to two kind of hollow sites at the surface. The hcp hollow sites differ from the fcc hollow sites in being directly located above a subsurface metal atom of the second layer. Adsorbates directly above surface atoms are in a top position and the site between two surface atoms is called bridge position.

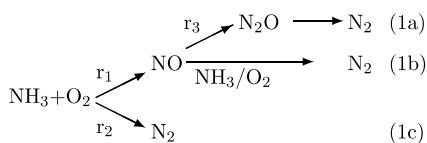


Fig. 1. Kinetic reaction scheme.

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